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Date: March 23, 2007 Rebecca A. Bellas
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of:

Applicant(s): Avanzino

Examiner: Mahmoud Dahimene

Serial No: 10/726,992

Art Unit: 1765

Filing Date: December 3, 2003

Title: SOLUTIONS FOR CONTROLLED, SELECTIVE ETCHING COPPER

Mail Stop Appeal Brief – Patents
Commissioner for Patents
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SECOND APPEAL BRIEF

Dear Sir:

Appellants' representative submits this brief in connection with an appeal of the above-identified patent application. This Second Appeal Brief responds to the Notice mailed February 23, 2007 indicating that the original Appeal Brief was non-compliant. In the event any additional fees may be due, the Commissioner is authorized to charge such fees to Deposit Account No. 50-1063 [AMDP1007US].

I. Real Party in Interest (37 C.F.R. §41.37(c)(1)(i))

The real party in interest in the present appeal is Advanced Micro Devices, Inc., the assignee of the present application.

II. Related Appeals and Interferences (37 C.F.R. §41.37(c)(1)(ii))

Appellants, appellants' legal representative, and/or the assignee of the present application are not aware of any appeals or interferences which may be related to, will directly affect, or be directly affected by or have a bearing on the Board's decision in the pending appeal.

III. Status of Claims (37 C.F.R. §41.37(c)(1)(iii))

Claims 1-20 stand rejected by the Examiner. The rejection of claims 1-20 is being appealed.

IV. Status of Amendments (37 C.F.R. §41.37(c)(1)(iv))

No claim amendments were made subsequent to the Final Office Action dated June 5, 2006.

V. Summary of Claimed Subject Matter (37 C.F.R. §41.37(c)(1)(v))

Independent Claim 1

Independent claim 1 recites a method of etching a copper containing material containing at least about 10 % by weight copper. The method involves two distinct acts. First, the copper containing material is contacted with a first solution to convert at least a portion of the copper containing material to a passivating film. The first solution contains a peroxide compound, a first organic acid, and water and has a pH from about 2 to about 6. Second, the passivating film is then contacted with a second solution to remove the passivating film. The second solution contains a second organic acid and water. (See e.g., page 3, lines 3-9, page 4, line 19, and page 6, lines 1-2).

Independent Claim 10

Independent claim 10 recites a method of etching a copper structure containing at least about 25 % by weight copper on a wafer. The method involves three acts. First, the copper structure is contacted with a first solution to convert at least a portion of the copper structure to a passivating film. The first solution contains a peroxide compound, a first organic acid, and water and has a pH from about 2 to about 6. Second, the passivating film is contacted with a second solution to remove the passivating film. The second solution contains a second organic acid and water, and the second solution has a lower pH and a higher temperature than the pH and temperature of the first solution. And third, the wafer is rinsed with water to provide the etched copper structure. (See *e.g.*, page 3, lines 3-9, page 4, line 22, page 6, lines 1-2, page 10, lines 12-13 and 25-26, and page 12, line 11).

Independent Claim 17

Independent claim 17 recites a method of etching a copper containing material. The method involves contacting the copper containing material with a first solution to convert at least a portion of the copper containing material to a passivation layer. The first solution contains a peroxide compound, a first organic acid, and water and has a pH from about 2 to about 6. The passivation layer is then contacted with a second solution to remove the passivation layer. The second solution contains a second organic acid and water. The method also involves simultaneously monitoring the formation and removal of the passivation layer using a scatterometry system. The scatterometry system functions by generating a signature associated with forming and removing the passivation layer, comparing the signature to a signature library to determine passivation layer depth, and terminating forming and removing the passivation layer when a desired depth is attained. (See *e.g.*, page 3, lines 3-17, page 6, lines 1-2, and Figures 4-6).

VI. Grounds of Rejection to be Reviewed (37 C.F.R. §41.37(c)(1)(vi))

- A.** Whether Uozumi and Kondo establish a *prima facie* case of obviousness for claims 1-3, 5, 7-11, 14, and 16 under 35 U.S.C. § 103(a).
- B.** Whether Uozumi, Kondo, and Miller establish a *prima facie* case of obviousness for claim 12 under 35 U.S.C. § 103(a).
- C.** Whether Uozumi, Kondo, and Shimazu establish a *prima facie* case of obviousness for claim 13 under 35 U.S.C. § 103(a).
- D.** Whether Uozumi, Kondo, and Singh establish a *prima facie* case of obviousness for claims 17-20 under 35 U.S.C. § 103(a).
- E.** Whether Uozumi, Kondo, and “admitted prior art” establish a *prima facie* case of obviousness for claims 4, 6, and 15 under 35 U.S.C. § 103(a).

VII. Argument (37 C.F.R. §41.37(c)(1)(vii))**A. One Skilled in the Art Would Not Have Modified Uozumi in the Manner Proposed by the Examiner**

Claims 1-3, 5, 7-11, 14, and 16 stand rejected under 35 U.S.C. § 103(a) over Uozumi in view of Kondo. Uozumi relates to forming a copper oxide film on a copper surface using an ammonia-hydrogen peroxide solution having a pH of 8-10, then removing the copper oxide film with a solution having a weak oxidizing property such as a diluted hydrochloric acid solution. The copper oxide film contains an ammonia complex. Uozumi clearly teaches that the presence of ammonia is important (see Col. 10, line 38).

Kondo relates to a polishing method for metal films involving mechanically rubbing a metal surface with an oxidizer (such as hydrogen peroxide) and a substance which renders oxides water soluble (such as inorganic or organic acids). However, in the Background section, Col. 5, lines 17-31 describes polishing solutions containing either citric acid or aminoacetic acid and hydrogen peroxide. Figure 26 and Figure 9 of Kondo show corrosion rates (etch rates) and passivation rates (formation of copper oxide) of the citric acid-hydrogen peroxide polishing solution and the aminoacetic acid-hydrogen peroxide polishing solution.

The first contention of the Examiner is that it would have been obvious to replace the ammonia-hydrogen peroxide solution of Uozumi with the citric acid-hydrogen peroxide polishing solution of Kondo to provide a wider range of stability for etch process, as taught by Figure 26 of Kondo. The Examiner notes that the sharp rise in etch rate versus pH for the ammonia-hydrogen peroxide solution of Uozumi as shown in Figure 6 is not desirable for process control.

The second contention of the Examiner is that it would have been obvious to use an organic acid of Kondo in the second solution of Uozumi because Kondo indicates copper and copper oxide are rendered water soluble thereby.

Applicants respectfully disagree with both contentions made by the Examiner for several reasons. Essentially, there would have been no motivation for one skilled in the art to make the modifications proposed by the Examiner to either the first solution or the second solution of Uozumi.

The First Contention

It would NOT have been obvious to replace the ammonia-hydrogen peroxide solution of Uozumi with the citric acid-hydrogen peroxide polishing solution of Kondo because 1) it would fundamentally change the process of Uozumi, 2) Kondo counsels using a CORROSIVE solution to achieve high etch rates for removing large amounts of material while the claimed invention has an absolute requirement of a PASSIVATION solution to achieve fine control over the removal of small amounts of material, and 3) Kondo directly TEACHES

AGAINST the use of a citric acid-hydrogen peroxide solution for the purposes of forming an insoluble passivation layer.

The basic, fundamental two step process of Uozumi involves forming a copper oxide film that contains an ammonia complex, and then removing the copper oxide film using a dilute acid with a weak oxidizing property. The citric acid-hydrogen peroxide polishing solution of Kondo, as taught by Figure 26, etches copper. That is, the corrosion rate is the rate at which copper is etched. The citric acid-hydrogen peroxide polishing solution of Kondo does NOT generate copper oxide. Generating copper oxide is the passivation rate. Since the citric acid-hydrogen peroxide polishing solution of Kondo would NOT generate a copper oxide film, on which the process of is predicated, substituting the citric acid-hydrogen peroxide polishing solution of Kondo for the ammonia-hydrogen peroxide solution of Uozumi would fundamentally change the process of Uozumi. One skilled in the art would have no motivation to modify the basic two step process of Uozumi when a passivation layer of CuO is required to practice the invention as discussed above. For at least this reason, the alleged combination fails to establish a *prima facie* case of obviousness.

Second, the fundamental purpose of Kondo is teaching the use of CORROSIVE solutions. This teaching is advantageous to the application of Kondo of etching relatively large amounts of material (about 800 nm) in a short time period as a corrosive solution has a high rate of etching. Such a high rate of etching is not required (50 nm/min) to achieve the fine degree of etching of the claimed invention. In fact, such a high rate of etching would be DELITERIOUS to etching on the angstrom scale, which the claimed invention is directed to.

Third, Figure 9 of Kondo teaches that passivation of copper may only be achieved from approximately pH 7 to pH 12. This directly teaches against the use of an organic acid-peroxide solutions to achieve passivation and an insoluble CuO layer since such a solution would have a pH less than 7, as the first solution of the claimed invention does. However, the nature of such Pourbaix diagrams change depending on the nature of the system. Specifically, ionic strength, detergents, and presence of certain ions such as ammonium modify the location

of boundary lines of the Pourbaix diagram for copper. There is no suggestion in Kondo that a passivation layer may be formed using an acidic solution.

Therefore, one skilled in the art could not use Kondo to make an acidic passivation solution as disclosed in Examples 1 to 4 of the invention. Note that the make-up of the preferred embodiments in Examples 1 to 4 are unique in their make-up compared to both Uozumi and Kondo and are intentionally designed to form a passivation layer at acidic pH. This function is claimed in claims 1, 10, and 17. One skilled in the art could not infer the composition of these solutions from the teaching of Uozumi or Kondo, either separately or combined, as neither suggests how to form a passivating solution at acidic pH.

The Examiner further contends that “it would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the teachings of Uozumi of a two-step process for etching copper by replacing the solutions used in both steps with new solutions provided the new solutions yield better results.” As discussed, the citric acid-peroxide solution of Kondo does NOT achieve the same result as the first solution of the invention.

The solution disclosed in Kondo is corrosive and capable of etching copper on its own. The first solution of the claimed invention forms a passivating film and is not capable of etching copper. These two solutions have different functions. A solution that does not perform the required function of passivating copper (as the solution in Kondo does not) can hardly be said to “yield a better result.”

A solution with properties of the first solution of the claimed invention is simply not disclosed anywhere in Kondo nor Uozumi. Further, the computer-controlled process of the claimed invention (claim 17, for example) requires a chemical process where the formation of a passivation layer of CuO can be observed through spectroscopic techniques. The method also requires monitoring of pH, temperature, and other physical parameters. The method is sensitive enough to stop the passivation process at a point to achieve chemical modification of less than 150 Å of material. The spectroscopic detection relies on the inherently different spectroscopic properties of Cu and CuO, and depth of

passivation is determined by measuring the formation of CuO. A process that calls for a corrosive solution that directly etches Cu off the surface would not be able compatible with this computer controlled technique as the direct removal of Cu into solution would not be able to be monitored and would not indicate how the surface has been modified. Therefore, there would have been NO motivation to incorporate any of the methods of Kondo into the current invention.

The Examiner specifically contends that the variation in etch rate with pH shown in Fig. 6 of Uozumi provides a motivation to modify the technique of Uozumi with that disclosed in Kundo to achieve greater pH stability. The fine computer control process of the current method makes a prior knowledge of the precise rate of etching IRRELEVANT for process control given the real-time monitoring of the passivation rate. The process also provides for real-time pH monitoring and adjustment which further makes any pH dependence of passivation rate IRRELEVANT. The processes of Kondo and Uozumi are not designed to be used in conjunction with real-time monitoring. Concerns over pH dependence would therefore not motivate one skilled in the art to modify the process of Uozumi.

The purpose of the second solution of Uozumi is to etch or remove a copper oxide film. Since citric acid-hydrogen peroxide polishing solution of Kondo does NOT generate a copper oxide film, substituting the citric acid-hydrogen peroxide polishing solution of Kondo for the ammonia-hydrogen peroxide solution of Uozumi would obviate the use of the second solution of Uozumi. One skilled in the art would NOT have undermined the purpose of the ammonia-hydrogen peroxide solution of Uozumi (forming a copper oxide film) by using a polishing solution that cannot form a copper oxide film.

For at least these reasons, it would NOT have been obvious to replace the first solution of Uozumi with the citric acid-hydrogen peroxide polishing solution of Kondo. It is believed that the comments above are sufficient to merit reversal of the rejections. Nevertheless, the following comments are also provided.

The Second Contention

It would NOT have been obvious to modify the second solution of Uozumi as suggested by the Examiner because the modification would contradict the basic requirements of the second solution of Uozumi.

It would not have been obvious to use an organic acid of Kondo or the acetic acid mentioned in the Background section of Uozumi in the second solution of Uozumi because such a modification contradicts a direct teaching of Uozumi. Uozumi clearly states that the second solution contains a weak oxidizing property. This is because the copper oxide film formed by the first solution of Uozumi is removed with a solution having a weak oxidizing property, such as a diluted hydrochloric acid solution (see Col. 9, line 51 of Uozumi). Organic acids, such as those required by the claimed invention, have NO oxidizing properties. Acids with oxidizing properties are inorganic or mineral acids. Thus, in the context of this technology, inorganic acids and organic acids are NOT equivalent (that is, inorganic acids and organic acids are not interchangeable). One skilled in the art would readily understand this, and consequently one skilled in the art would not have used an organic acid of Kondo or the acetic acid mentioned in the Background section of Uozumi to replace the second solution of Uozumi.

Since the acetic acid mentioned in the Background section of Uozumi is clearly known by Uozumi, Uozumi would have mentioned acetic acid as a possible acid with a weak oxidizing property if such were suitable and interchangeable with its second solution. For the reasons stated in the preceding paragraph, Uozumi made no mention of this "potential" interchangeability because the function of its second solution would be lost. For these additional reasons, reversal of the rejection is respectfully requested.

Summary

Absent the guidance provided by the instant specification, one skilled in the art would not have modified Uozumi as proposed by the Examiner. There is simply no motivation to contradict or undermine the clear teachings Uozumi (and

thereby twist the intentions of Uozumi). The teachings of Kondo are not compatible with the objectives of Uozumi.

B. All Dependent Claims May Stand or Fall With Their Respective Independent Claims

Claim 12 stands rejected under 35 U.S.C. § 103(a) over Uozumi in view of Kondo and further in view of Miller. Due to the deficiencies of Uozumi and Kondo described in section A of this appeal brief, claim 12 is patentable for the same reasons that claim 1 is patentable.

C. All Dependent Claims May Stand or Fall With Their Respective Independent Claims

Claim 13 stands rejected under 35 U.S.C. § 103(a) over Uozumi in view of Kondo and further in view of Shimazu. Due to the deficiencies of Uozumi and Kondo described in section A of this appeal brief, claim 13 is patentable for the same reasons that claim 1 is patentable.

D. All Dependent Claims May Stand or Fall With Their Respective Independent Claims

Claims 17-20 stand rejected under 35 U.S.C. § 103(a) over Uozumi in view of Kondo and further in view of Singh. Due to the deficiencies of Uozumi and Kondo described in section A of this appeal brief, claims 17-20 are patentable for the same reasons that claim 1 is patentable.

E. All Dependent Claims May Stand or Fall With Their Respective Independent Claims

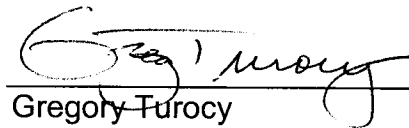
Claims 4, 6, and 15 stand rejected under 35 U.S.C. § 103(a) over Uozumi in view of Kondo and further in view of admitted prior art. Due to the deficiencies of Uozumi and Kondo described in section A of this appeal brief, claims 4, 6, and 15 are patentable for the same reasons that claim 1 is patentable.

F. Conclusion

For at least the above reasons, the claims currently under consideration are believed to be patentable over the cited references. Accordingly, it is respectfully requested that the rejections of claims 1-20 be reversed.

If any additional fees are due in connection with this document, the Commissioner is authorized to charge those fees to Deposit Account No. 50-1063 [AMDP1007US].

Respectfully submitted,
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VIII. Claims Appendix (37 C.F.R. §41.37(c)(1)(viii))

1. (previously presented) A method of etching a copper containing material, comprising:

contacting the copper containing material comprising at least about 10 % by weight copper with a first solution to convert at least a portion of the copper containing material to a passivating film, the first solution comprising a peroxide compound, a first organic acid, and water and having a pH from about 2 to about 6; and

contacting the passivating film with a second solution to remove the passivating film, the second solution comprising a second organic acid and water.

2. (original) The method of claim 1,

the peroxide compound is selected from the group consisting of one or more of barium peroxide, benzoyl peroxide, carbamide peroxide, cumene hydroperoxide, di-t-butyl peroxide, hydrogen peroxide, potassium peroxide, and sodium peroxide; and

the first organic acid and the second organic acid independently selected from the group consisting of one or more of formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, perfluoroacetic acid, perfluorooctanoic acid, oxalic acid, malonic acid, succinic acid, fumaric acid, glutaric acid, itaconic acid, ethylenediaminetetraacetic acid, citric acid, ascorbic acid, maleic acid, malic acid, dimethylphosphoric acid, dimethylphosphinic acid, methanesulfonic acid, trifluoromethanesulfonic acid, ethanesulfonic acid, 1-pentanesulfonic acid, 1-hexanesulfonic acid, 1-heptanesulfonic acid, benzenesulfonic acid, benzenedisulfonic acid, toluenesulfonic acid, naphthalenesulfonic acid, tropolone, benzoic acid, and picric acid.

3. (original) The method of claim 1, wherein the first solution comprises from about 1 % to about 50 % by weight the peroxide compound, from about 0.001 % to about 10 % by weight of the first organic acid, and from about 30 % to about 98 % by weight of water.

4. (original) The method of claim 1, wherein the first solution further comprises at least one of a surfactant, a pH adjuster, and an ionic salt.

5. (original) The method of claim 1, wherein the second solution comprises from about 0.001% to about 10% by weight of the second organic acid and from about 50 % to about 99.9 % by weight of water.

6. (original) The method of claim 1, wherein the second solution further comprises at least one of a surfactant, a pH adjuster, and a biocide.

7. (previously presented) The method of claim 1, wherein the first solution has a pH from about 3 to about 5.5 and the second solution has a pH from about 1 to about 6.

8. (original) The method of claim 1, wherein the first solution has a temperature from about 5 °C. to about 50 °C. the second solution has a temperature from about 20 °C. to about 90 °C.

9. (original) The method of claim 1, wherein the passivating film comprises copper oxide.

10. (previously presented) A method of etching a copper structure, comprising:

contacting the copper structure comprising at least about 25 % by weight copper on a wafer with a first solution to convert at least a portion of the copper structure to a passivating film, the first solution comprising a peroxide compound, a first organic acid, and water and having a pH from about 2 to about 6;

contacting the passivating film with a second solution to remove the passivating film, the second solution comprising a second organic acid and water, the second solution having a lower pH and a higher temperature than the pH and temperature of the first solution; and

rinsing the wafer with water to provide an etched copper structure.

11. (original) The method of claim 10, wherein the first solution comprises from about 2 % to about 40 % by weight the peroxide compound, from about 0.01% to about 5% by weight of the first organic acid, from about 40% to about 95% by weight of water, from about 0.01 % to about 20 % by weight of a surfactant, and from about 0.001% to about 5% by weight of a pH adjuster.

12. (original) The method of claim 10, wherein the second solution comprises from about 0.01% to about 5% by weight of the second organic acid, from about 70% to about 99.5% by weight of water, from about 0.001% to about 5% by weight of a biocide, and from about 0.001% to about 5% by weight of a pH adjuster.

13. (original) The method of claim 10, wherein the second solution comprises at least two organic acids.

14. (original) The method of claim 10, wherein the first solution contacts the copper structure for a time from about 1 second to about 200 minutes and the second solution contacts the passivating film for a time from about 1 second to about 200 minutes.

15. (original) The method of claim 10, wherein the first solution further comprises a nonionic water soluble polymer surfactant.

16. (original) The method of claim 10, wherein the etched copper structure has an R_{tm} of about 50 Å or less.

17. (previously presented) A method of etching a copper containing material, comprising:

contacting the copper containing material with a first solution to convert at least a portion of the copper containing material to a passivation layer, the first solution comprising a peroxide compound, a first organic acid, and water and having a pH from about 2 to about 6;

contacting the passivation layer with a second solution to remove the passivation layer, the second solution comprising a second organic acid and water;

and simultaneously

monitoring the formation and removal of the passivation layer using a scatterometry system by generating a signature associated with forming and removing the layer, comparing the signature to a signature library to determine layer depth, and terminating forming and removing the passivation layer when a desired depth is attained.

18. (original) The method of claim 17, wherein generating the signature associated with forming and removing the passivation layer comprises directing a beam of incident light at the passivation layer, collecting light reflected from the passivation layer, and transforming the reflected light into the signature.

19. (original) The method of claim 17, wherein a closed loop feedback control system for terminating the formation and removal of the passivation layer according to the determined depth comprises feeding information related to passivation layer depth via the closed loop feedback control system to a first and second solution controller, wherein the first and second solution controller is connected to a trained neural network to facilitate termination of the formation and removal of the passivation layer.

20. (original) The method of claim 17, wherein the scatterometry system further compares the signature to a signature library to determine passivation layer profile, and terminates forming and removing the passivation layer when a desired passivation layer profile is attained.

IX. Evidence Appendix (37 C.F.R. §41.37(c)(1)(ix))

None.

X. Related Proceedings Appendix (37 C.F.R. §41.37(c)(1)(x))

None.